ELECTROOSMOSIS EFFECT ON MICRO PERMEABILITY
THROUGH ROCK SAMPLES

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ABSTRACT

It is a well known fact that a liquid flowing through a microporous media creates a potential difference between entry and exit of the sample. This phenomenon is known as streaming potential. In an other hand, when a potential difference is applied through an impregnate rock sample, a flow is induced, this is called electroosmosis effect. In this paper, we examine electroosmosis experiments made in a percolation cell in which two gold electrodes are placed in the inner and in the outer chamber. The temperature, the pressure and potential difference, the flow, the current and the chemical composition of water in chambers may be recorded.

Experiment consist to the application of electric field through the sample and to observe the evolution of the flow, the electrical current and the chemical dissolution.

THEORETICAL CONSIDERATIONS

At the interface between a liquid and a solid surface an electrical double layer appears whichever liquid and solid are in contact. This phenomenon is due to the specific adsorption process. Thus the ions or ionised impurities existing in the liquid are differently adsorbed on a solid surface, this leads to the development of a double layer, with two opposite kind of charge, one in the solid and one in the liquid.

By the past different model have been proposed for the double layer [1,2]. The most recent and realistic one is due to Stern [3] and predict in fact two different regions in the liquid : one very close to the wall is called the compact layer, the other one the diffuse layer. The thickness of the compact layer is very small (in the order of the ionic radius). In the diffuse layer ions are not fixed and subjected to the liquid motion, the concentration of charge is decreasing from the wall to the bulk of the liquid. A conventional thickness of this layer is called the Debye length it is conversely proportional to the square root of the electrical conductivity :

\[
\delta_0 = \frac{\sqrt{\varepsilon D_0}}{\sigma}
\]

where \( \sigma \) is the electrical conductivity, \( \varepsilon \) the permittivity of the liquid and \( D_0 \) the mean diffusion constant of ions.

When the difference between concentrations of positive and negative ions in a diffuse layer remains small compared to the mean value of the both concentrations, this situation is known as the case of weak space charge density [4].

In that case and for mono-valence cations and anions of same diffusion constant, the general equations for a fully developed diffuse layer at rest has analytical solutions [5], depending on the nature of the solid and the liquid and also on the geometry of the interface.

Thus for a plane wall in contact with a liquid the space charge density profile in the diffuse layer is given by the relation :

\[
\rho(x) = \rho_w e^{-x/\delta_0}
\]
where \( \rho(x) \) is the space charge density, \( \rho_w \) is the space charge density on the wall, \( x \) the distance to the wall and \( \delta_0 \) the diffuse layer thickness.

In the case of two infinite parallel walls separated by a liquid layer the space charge density profile is symmetrical, smallest on the medium plane and growing close to the walls:

\[
\rho(x) = \rho_w \frac{\text{ch}(x/\delta_0)}{\text{ch}(a/\delta_0)}
\]

(3)

where \( x \) is the distance from the medium plane and \( a \) the separation between the two planes.

In the case of a pipe of circular cross section the solution can be expressed in terms of Bessel functions:

\[
\rho(r) = \rho_w \frac{\text{I}_0(r/\delta_0)}{\text{I}_0(R/\delta_0)}
\]

(4)

\( r \) being the radial co-ordinate from the axis of the pipe and \( R \) the pipe radius. \( \text{I}_0 \) is the modified Bessel function of the zero order.

For a microporous media we often consider that the sample can be assumed as a set of parallel pipes, the radii of which being equal to the pores ones.

When a pressure gradient is applied through an impregnated rock sample the liquid flows through the rock. Thus taking the previous "pipe model" for the sample we can assumed that at the entrance of the pipes set the liquid is electrically neutral, then due to the specific adsorption phenomenon the electrical double layer develops and if the sample is thick enough at the exit the diffuse layer is fully developed.

Thus the space charge convected by the flow is obtained from integration of the product of the space charge density profile by the flow velocity.

\[
Q = \int_0^R 2\pi r \rho(r) U(r) dr
\]

(5)

where \( U(r) \) is the velocity profile in the pipe and \( \bar{U} \) the mean velocity.

As the flow is generally very low it is laminar and the velocity profile is given by:

\[
U(r) = 2\bar{U} \left(1 - \frac{r^2}{R^2}\right)
\]

(6)

Thus:

\[
Q = \frac{4}{R^2} \int_0^R 4\rho_w \frac{\text{I}_0(r/\delta_0)}{\text{I}_0(R/\delta_0)} rdr
\]

(7)

Then the streaming current for the microporous sample is given by:

\[
I_s = Q.F
\]

(8)

where \( F \) is the mean flow through the sample and \( Q \) the space charge density convected [6]:

\[
Q = 8\rho_w \frac{\delta_0^2}{R^2} \left[1 - \frac{2\delta_0 \text{I}_1(R/\delta_0)}{\text{RI}_0(R/\delta_0)}\right]
\]

(9)

(\( \text{I}_1 \) is the modified bessel function of 1st order)

This current leads to a potential between the entry and exit face of the sample and is counter balanced by a back current due to the conductivity [7]:

\[
V_s = I_s.Rc
\]

(10)

where \( R_c \) is the resistivity of the whole impregnate media. This streaming potential may easily be measure by means of electrodes close to the exit and entry faces of the sample.

In the opposite case when no pressure gradient is applied but a potential difference between the electrodes, an electrical force acts on the liquid inside the sample due to the product of the electric field and the space charge density existing in the diffuse layer. This force is more important close to the wall as the space charge density is higher. Thus for a model of a pipe of circular cross section again. The applied electric field induced a motion of the liquid in the same direction that the field.
Fig. 1. General diagram of the equipment.

Fig. 2. Permeability cell.
EXPERIMENTS

We see Fig. 1 the general set up for electropermeability through rock samples, on Fig. 2 the permeability cell is shown more in details. The samples shape is given Fig. 3, as the electrical diagram of the electroosmosis experiments in Fig. 4.

![Fig. 3. Shape and dimensions of the rock samples](image)

![Fig. 4. Electrical diagram for electroosmosis experiments.](image)

It is in fact an equipment built for micro permeability measurement which has been adapted for electrical measurements. It is composed of a cell made in PEEK (1). This material has been chosen for both thermal and electrical considerations, as it is a good electrically insulating material and much more rigid for high temperature than PTFE for example. The sample has a conic form and is pressed in a conic sample holder in order to avoid any leak. The holder is then introduce in the cell. The liquid flows between two big stainless steel reservoirs (2) through the cell and the flow visualisation system.

The whole cell may me introduced in an oven for experiment in terms of temperature. The flow visualisation system is a simple glass tube of 5 mm of diameter and in which meniscus is carefully observed by means of a cathetometer.

Inside the cell two gold electrodes placed in the entry and exit chambers at about 2 mm of the sample faces, are connected to a power DC supply through a microammeter.

The rock sample has a diameter around 3 cm with a difference of 2 mm between entry and exit faces (conic shape), it is 1.4 cm thick.

Analysis of liquid composition can be made before and after experiments and in both chambers.

We relate in this paper two kind of experiments one made with a limestone sample and the other one with a basalt sample.

EXPERIMENTS WITH LIMESTONE

The electrical resistivity of the dry sample is first measured inside a special conductivity cell performed in the laboratory, we found a resistance around $10^9 \, \Omega$.

Then the sample is introduced in the permeability cell and a normal permeability experiment is carried on at a temperature of 25°C. Thus a confining pressure of 5 bars is applied with a difference of 0.5 bars between the two faces. The flow velocity through the sample is recorded Fig. 5 it is of the order of $4.5 \times 10^{-1} \, \text{mm}^3/\text{s}$. After the experiments chemical analysis of water in the exit chamber shows an important calcium concentration (497 mg/l).

![Fig. 5. Flow velocity through a limestone sample under 0.5 bar of pressure difference.](image)
A new experiment is then made that time no pressure gradient exists between the two chambers but a potential difference of 30 V is applied between the gold electrodes. The current and the flow velocity are recorded. We can see Fig. 6 that the current is slowly increasing from $4.9 \times 10^{-3}$A to $5.3 \times 10^{-3}$A. This is probably due to the evolution of the concentration of calcium in the liquid.

During the experiment no gas have been produced by electrolysis and the analysis of calcium in the exit chambers give (416 mg/l) (same order than previously). In first analysis of this experiment we see that a potential difference of 30 V give the same flow than 0.5 bar of pressure difference, the chemical concentration in water seems to be not affected by the electrical phenomenon.

**EXPERIMENTS WITH BASALT**

We made experiments with different samples of basalt taken from Fangataufa which is an atoll in the archipelago of TUAMOTU in French Polynesian. It has been taken at 745 m below the see level, and has a very weak alteration.

The different basalt samples chosen for the experiment have been selected for a quasi null permeability. Indeed each sample have been placed in the permeability cell under a confining pressure of 10 bars at 140°C and 1 bar difference between entry and exit faces. After one day of pressure gradient application the flow is not detectable (i.e. if the liquid has past through the rock the total amount after one day is less than 1 mm$^3$). Thus two configurations can exist: the porosity is not interconnected or the connections are so narrow (close to the water molecule diameter) than the mechanic of continuum media is not applicable.

We were interested to know which configuration really exist and what can be the effect of electric field on selective migration of ions through the rock. For that we made three different experiments with a solution of lithium chloride.

In all experiments the entry chamber was filled with a solution of lithium chloride (2100 mg/l) and the exit chamber with pure water. The confirming pressure was 1 bar and the temperature 25°C.

For the two first experiments the basalt sample was previously impregnated by a lithium chloride solution during several days.

The first experiment is made without field. After 4 days we analysed the concentration of lithium in both chambers. In this experiment only diffusion is acting and we can see on Table 1 that only a very small amount of lithium has diffused.
In the second experiment a potential difference of 500 volts is applied between entry and exit chambers. The current recorded Fig. 8. increases first and then decreases. Hydrogen gas appeared (6.7 cm$^3$) in the exit chamber but no flow was noticed. At the end of the experiment the concentration in lithium in the entry chamber was only (1160 mg/l) but 95.9 mg/l appeared in the exit chamber (Table 1).

At least a third experiment was carried on with a basalt sample impregnated in pure water and with a potential difference of only 50 V but during 48 hours.

The current is increasing (Fig. 9.), we noticed again no flow but a hydrogen gas production in the exit chambers. The concentration of lithium is at the end of the experiment nearly the same than in the second experiment (Table 1).

**DISCUSSION**

The application of an electric field in the case of nearly impermeable basalt sample does not induced a real permeability (no flow) but a kind of "selective permeability" which is in fact a migration of ions under electric field. This is possible if the porosity of basalt is interconnected but with very narrow channels.

The fact to try to impregnate basalt sample by diving it several days in a solution seems to be not efficient as the results are nearly the same for the two different cases.

**CONCLUSION**

The effect of an applied electric field to a basalt sample nearly impermeable gives very interesting results has it induced selective permeability due to electric migration of one kind of ions through the sample. The effect of the electric field is much more important that the simple diffusion of ions through the rock. It is obvious that several applications of
this phenomenon may be considered for environment.

REFERENCES